

Homogeneous TIP4P/2005 ice nucleation at low supercooling

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Although homogeneous ice nucleation is thought to be an important process in atmospheric science¹ and understanding how ice grows has recently been identified as one of the top open questions in ice science,² simulating the process has been fraught with difficulties.^{3–6} This is especially the case for all-atom model simulations, since water dynamics at significant supercoolings are very slow indeed,⁶ which has made the determination of free energy landscapes and nucleation rates using such models very difficult.⁶ One approach that could provide some insight into the process, while still being computationally tractable, would be to simulate homogeneous nucleation using the TIP4P/2005 model of water⁷ at temperatures at which the dynamics are reasonably fast and at which equilibration can thus be achieved, at least for relatively small crystalline nuclei.

We have run simulations analogous to those presented in Ref. 6 using hybrid Monte Carlo⁸ with adaptive umbrella sampling⁹ and a local order parameter to drive the process.⁶ These simulations started with seed hexagonal and cubic ice crystals at 240 K and 1 bar, which is a $\sim 5\%$ supercooling for TIP4P/2005 water. The starting umbrella weights corresponded to the negatives of the free energy barrier estimated from classical nucleation theory (CNT).¹⁰ A free energy profile for nucleation from such simulations is shown in Fig. 1. Whilst the range of crystalline cluster size presented here is rather limited (e.g., the critical cluster predicted by CNT is of the order of 1.5×10^4 molecules), even the calculation of just this set of free energies represents a huge computational effort, as even at such small supercoolings, the dynamics of ice growth are slow on computational time scales. Consequently, obtaining more complete data would be prohibitively expensive, particularly for larger cluster sizes for which larger system sizes would need to be simulated.

To test whether equilibrium has been attained, we need to ensure that there is sufficient sampling and frequent exchange across order parameter values. We can also calculate the enthalpy as a function of the order parameter and ensure that it behaves sensibly. These equilibration criteria are fulfilled by the simulations whose results are presented in Fig. 1, and so we have obtained equilibrium results for ice nucleation at low supercoolings. We remark that the reason for the deviation from the trend at the extreme cluster size values is due to windowing errors, which are especially significant when instantaneous order parameter values can fluctuate to the extent that they can in these systems.⁶

If we fit the simulation data shown in Fig. 1 to a CNT-like expression for the Gibbs energy, as we did when studying ice nucleation⁵ using the mW monatomic model of water,¹¹ we find that $\Delta_{\text{fus}}\mu(240\text{K})/k_B \approx 29.3\text{ K}$ and $\gamma \approx 24.0\text{ mJ m}^{-2}$; these values compare favourably to the $\Delta_{\text{fus}}\mu(240\text{K})/k_B \approx 27.7\text{ K}$ estimated using the approximation that $N\Delta_{\text{fus}}\mu \approx$

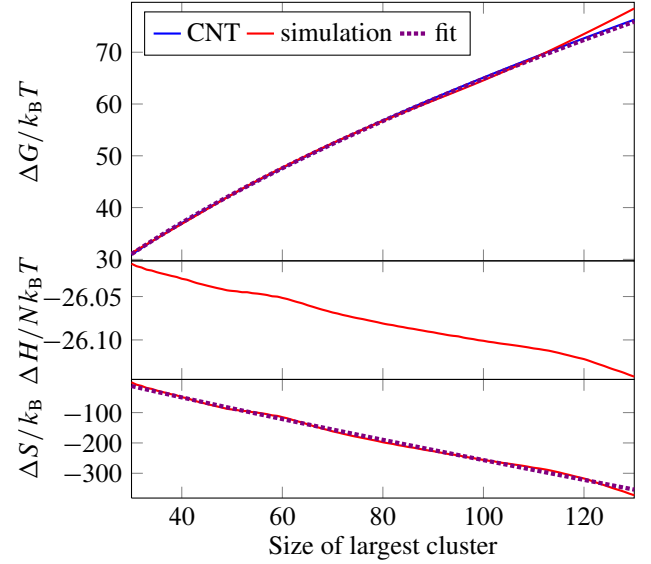


FIG. 1. The Gibbs energy, enthalpy and entropy for TIP4P/2005 ice nucleation as a function of the size of the largest crystalline cluster for systems seeded with a cubic ice seed. The hexagonal nucleation seed simulation results are analogous. $T = 240\text{ K}$, $p = 1\text{ bar}$, $N = 2500$ molecules. In the top panel, the simulation result is shifted so that it matches the CNT estimate at size 50, and this estimate is also shown. In the bottom panel, the curve is shifted so the simulation ΔS is zero at a size of 30.

$\Delta_{\text{fus}}H(1 - T/T_{\text{fus}})$ and $\gamma \approx 24.5\text{ mJ m}^{-2}$ calculated for the basal plane of TIP4P ice.¹² The simulation results appear to agree very well with the CNT prediction; indeed, the agreement is almost suspiciously good. Given that we started the simulations with umbrella weights corresponding to CNT, we could envisage a situation where the clusters essentially remain at their original size because of the slow dynamics of the ice cluster growth/shrinkage process. While this is certainly always a conceivable issue in simulations of water, it does not appear to be a problem in these high-temperature simulations, since in equivalent simulations with starting weights corresponding to CNT weights at 235 K and at 245 K (with the simulation temperature remaining at 240 K), clusters were observed to shrink over time with the former and to grow with the latter set of umbrella weights. This suggests that the CNT estimate at the temperature of simulation does in fact yield a reasonable approximation to the free energy barrier associated with the simulated process. However, the good agreement in this very early stage of the nucleation process is no guarantee that the critical cluster size or the height of the free energy barrier to

nucleation are also well estimated by CNT.

It is also interesting to note that the enthalpy associated with the growth of the crystal nucleus is a monotonically downhill function of the nucleus size (Fig. 1); this result implies that, analogously to the mW simulation results,⁵ the barrier to nucleation is primarily entropic in nature. This suggests that the formation of an ice-liquid surface is enthalpically favourable (or at least neutral), but entropically unfavourable. Since $(\partial\gamma/\partial T)_p = -S_{\text{interface}}$, where $S_{\text{interface}}$ is the entropy change per unit area upon the formation of an interface, this finding is consistent with experiment, where the interfacial free energy was found to decrease with temperature.¹³ We can attempt to quantify this temperature dependence to first order by explicitly evaluating this interfacial entropy. To do this, we first find $\Delta S(n)$, where n is the number of molecules in the largest crystalline cluster, by using $\Delta G(n)$ and $\Delta H(n)$ determined from the simulation (Fig. 1). We then proceed to fit these values to $\Delta S(n) = an + bn^{2/3} + cn^{1/3} + d$, where a is constrained to be the bulk entropy change at coexistence (namely $a = \Delta_{\text{fus}}S/N = \Delta_{\text{fus}}H/NT_{\text{fus}}$, where $T_{\text{fus}} = 252\text{ K}$), and we assume that $b = S_{\text{interface}}(36\pi/\rho_{\text{ice}}^2)^{1/3}$, where the factor $(36\pi/\rho_{\text{ice}}^2)^{1/3}$ accounts for the assumed spherical shape of the clusters. This gives a value of $S_{\text{interface}}$ of $-0.18\text{ mJ m}^{-2}\text{ K}^{-1}$, and also allows us to estimate the interfacial enthalpy, defined by $H_{\text{interface}} = \gamma + TS_{\text{interface}}$, as -18.6 mJ m^{-2} . Integrating $(\partial\gamma/\partial T)_p = -S_{\text{interface}}$ with respect to the temperature, assuming that the entropy is independent of temperature, gives an interfacial free energy at coexistence of 26.1 mJ m^{-2} . This is reasonably consistent both with the mean values obtained by Davidchack and co-workers for TIP4P water,¹² as well as the TIP4P/2005 estimate of $\gamma \approx 28\text{ mJ m}^{-2}$ obtained from CNT critical cluster size fits for small supercoolings.¹⁴ The relative agreement between these different approaches to obtaining γ is interesting, given the contrasting behaviour for systems such as NaCl.¹⁵ However, it should be borne in mind that our estimates are rather crude, as we (a) assume that classical nucleation theory applies, (b) calculate non-linear fits to the data, where a variety of fits is likely to lead to reasonable agreement, and (c) extract these data from a relatively small range of cluster sizes.

In their work, Limmer and Chandler calculate an estimate of the interfacial free energy and its variation with temperature for the mW model of water.¹⁶ They demonstrate that for the mW model, the Turnbull relation, $\gamma(T_1)/\Delta_{\text{fus}}H(T_1) = \gamma(T_2)/\Delta_{\text{fus}}H(T_2)$,¹⁷ works remarkably well. If we assume that the same relation applies to TIP4P/2005 water and that $\gamma(240\text{ K})$ as reported above is correct, and we obtain $\Delta_{\text{fus}}H(T)$ from fits to the internal energy and density of ice and liquid water found in the literature,¹⁸ we find that $\gamma(252\text{ K}) \approx 27.5\text{ mJ m}^{-2}$, again in reasonable agreement with our estimate for this temperature.

In summary, we have presented the first results for the free energy profile associated with the homogeneous nucleation of ice using a rotationally invariant local orientational order parameter for an all-atom model of water. These low supercooling results corroborate our hypothesis^{5,6} that for ice nucleation, classical nucleation theory predictions may be considerably better than might initially be assumed; this is consistent with

the results of Ref. 14. We note that the free energy barriers obtained in some previous simulations,³ which were significantly larger than the CNT estimate, likely arise from the use of global order parameters, which can result in nucleation pathways that are not the lowest in free energy in systems with slow dynamics.⁶ Furthermore, we have shown here that the interfacial entropy is negative: presumably, the hydrogen bonding of liquid molecules with the ice nucleus considerably constrains the hydrogen bond network in the liquid near the surface. However, our attempts to determine the overall free energy barrier and nucleation rate of homogeneous ice nucleation using all-atom models of water have been thwarted by the slow dynamics of the system. We note that despite our attempts to circumvent this difficulty, such as using histogram reweighting and hamiltonian exchange,¹⁹ we have been unable to obtain simulation results at sufficiently low temperatures to enable us to calculate nucleation rates. The slow dynamics of ice growth at low temperatures thus continue to pose a very significant obstacle. The use of advanced simulation methods does offer new insights into the process; nevertheless, the successful calculation of ice nucleation rates for all-atom models of water continues to be a challenge.

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